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Gold sensitized sprayed SnO₂ nanostructured film for enhanced LPG sensing

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Abstract

We report LPG sensing of gold (Au)-sensitized SnO₂ nanostructured film fabricated by an easy spray pyrolysis deposition method whose surface morphology is confirmed by field-emission scanning electron microscopy and atomic force microscopy images and structure by X-ray diffraction pattern. Energy dispersive X-ray spectrometer analysis has carried out for finding elemental composition. The SnO₂ film is uniform and consists of spherical particles of ~10 nm. The highest gas response observed at 780 ppm LPG concentration for pristine SnO₂ is 28%, at operating temperature 623 K, which is greatly improved on Au sensitization up to 57% with 60 s rapid response time at 598 K operating temperature. The high gas response is due to electronic effect and catalytic spill-over effect of Au sensitization. The improved sensing mechanism has thoroughly been explored.

1. Introduction

The detection of inflammable and explosive gases has become an important area of research. The leakage of these gases can cause major explosions/accidents. The LPG, one of the highly inflammable and potentially hazardous gases is widely used in household, vehicle fuels and at the industry level. Nowadays accidents due leakage of LPG are significantly increasing. The accidental leakage of LPG has been increased awareness for efficient detection and constant monitoring. Taking into the account, there is need for high sensitivity and low concentration level detection of LPG. The nanocrystalline semiconducting metal oxide resistive gas sensors have attracted great attention for a long time, due to their low costs, ease of fabrication and high sensitivity towards various oxidizing and reducing gases [1]. The metal oxides like SnO₂ [2], TiO₂ [3], ZnO [4], and CdO [5] have been envisaged for gas sensing application. The SnO₂ is one

of the most promising materials that has been used as a gas sensor for the detection of a variety of gases [6]. Under the given operation conditions, SnO₂ based gas sensors find good chemical and thermal stabilities along with high mobility of conduction electrons [7]. The SnO₂ is most practically used device due to its excellent inherent property of the exchange of oxygen with atmosphere [8–10]. It is reported that gas sensitivity can be enhanced using the metal catalytic effect of noble metals like gold (Au) [11,12], platinum (Pt) [13–15], and palladium (Pd) [16–18]. The methods used for noble metal doping or surface sensitization/functionalization increases gas sensing performance. There is need of developing new methods for sensitization/functionalization of noble metal nanoparticles to improve gas sensing properties. Several methods have been followed for deposition of SnO₂ films such as aerosol-assisted chemical vapour deposition [19], pulsed laser deposition [20], RF sputtering [21], physical vapour deposition [22] etc. Spray pyrolysis deposition (SPD) has advantages such as it is very simple, economical, and no vacuum required, free from the high quality substrates or chemicals, formation of denser and porous films [23,24]. The Au sensitized SnO₂ film is prepared by SPD method. This Au sensitized SnO₂ film has evidenced enhanced LPG sensing properties in comparison with pristine SnO₂ film. In the present study, Au sensi-

tized SnO₂ films have used for LPG sensing properties. Synthesis of SnO₂ films (using stannic tetrachloride solution) with Au sensitization have done by SPD method. The nanostructured SnO₂ films, with and without Au-sensitization, have characterized for their morphologies; crystal structures and sensitization measurements. The LPG sensing responses for different operating temperatures and LPG concentrations are studied. Sensor stability is recorded. The transient response for LPG has also studied. The probable mechanism for enhancement in LPG sensing is discussed using schematics and band diagram.

2. Experimental

The SnO₂ films were deposited on glass substrate by SPD method using 0.3 M solution of stannic tetrachloride. The molar solution of stannic tetrachloride salt was prepared in the solvent i.e. distilled water: methanol (ratio 2:3). The prepared solution sprayed through a steel nozzle on to the ultrasonically cleaned glass substrate at 675 K. The distance between nozzle and glass substrate was fixed at 25 cm with 3 ml/min spray rate using air as the carrier gas. The temperature of glass substrates was controlled by using electronic PID temperature controller unit. The hazardous fumes generated from thermal decomposition of solution were expelled out via the exhaust. Deposited films were kept for 1 h on heater at deposition temperature to provide an additional crystallization. Au sensitization was done on the surface of SnO₂ using 0.001 M solution of HAuCl₄ · H₂O aqueous solution at 523 K by SPD method. All depositions were done by using Holmarc Opto-Mechatronics PVT. LTD. SPD system (model No. HO-TH-04). The Au sensitized and pure SnO₂ samples were used for their structural, morphological and optical properties initially and then employed for LPG sensing properties.

The phase formation of the SnO₂ sample was confirmed using X-ray diffractometer (XRD) with Cu-K α (wavelength = 1.5406 Å) radiation in the 2 θ range from 20 to 80°. Morphology of pristine and sensitized SnO₂ films was confirmed using field-emission scanning electron microscope (FE-SEM) and atomic force microscopy (AFM) digital images. Elemental composition was recorded by energy dispersive X-ray spectroscopy (EDS). To measure gas sensing properties, silver paint contacts with two copper rod electrodes on both films were fixed for electrical measurements. The test sample was kept in a sealed chamber and stabilized resistivity (R_a) of the SnO₂ film in the air was measured. Thereafter, LPG gas was injected into the chamber and resistivity of the sample after allowing sufficient time for equilibrium in the presence of LPG gas (R_g) was recorded. Since test chamber was sealed by keeping other gas sensing parameters constant, the change in resistivity of the sample was monitored on account of LPG exposure. The gas response formula used for sensor sensitivity measurement followed [5]

$$S = ((R_a - R_g)/R_a) \times 100\%. \quad (1)$$

The LPG sensing properties were studied by using a computer controlled system.

3. Results and discussions

3.1. Structural analysis

The X-ray diffraction patterns for SnO₂ and Au-SnO₂ films are as shown in Fig. 1. Peaks in pattern reveal confirmation of SnO₂ crystal structure [25]. The XRD peaks are also matched with standard PCPDF data PDF#721147, which confirms SnO₂ tetragonal structure. XRD peaks are sharp with good intensity, which shows high crystallinity and purity of SnO₂ sample however, peaks for Au in Au-SnO₂ XRD pattern are missing, this may be because of involvement

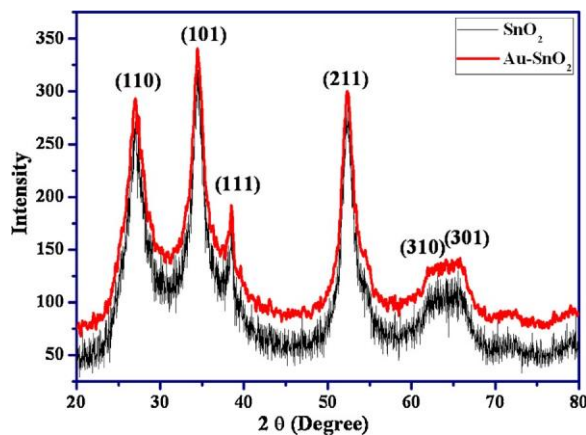


Fig. 1. The XRD patterns of the SnO₂ and Au-SnO₂ films.

of very less concentration of Au salt (0.001 M) used while sensitization as a result there are quite less number of Au nanoparticles on SnO₂ film. The less number of Au nanoparticles may not contribute in XRD pattern. The crystallite size of SnO₂ was calculated using Scherrer's formula as [26].

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

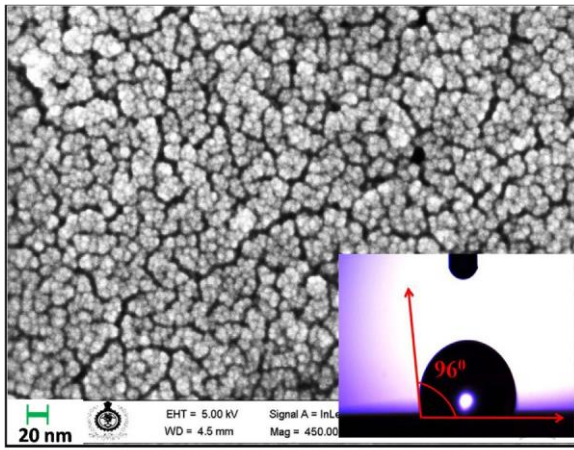
where, λ is the wavelength of X-ray, β is the full width at half maximum, θ is the Bragg's angle. The average crystallite size is estimated to be ~6 nm from the most intensive peak of XRD spectrum. The broad peaks in XRD pattern confirm smaller crystallite size of the SnO₂ film.

3.2. Morphological and elemental analysis studies

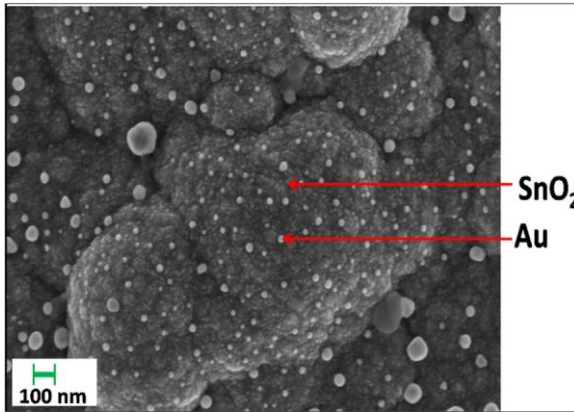
The two-dimensional (2-D) SnO₂ morphology studies have been carried out using FE-SEM. The FE-SEM micrograph images for SnO₂ and Au sensitized SnO₂ are shown in Fig. 2 a) and b), respectively. The spherical particle-like morphology with diameter below 10 nm is evidenced from Fig. 2a) which can provide the high surface to volume ratio by allowing a maximum number of surface atoms to participate in gas sensing reaction. The particles are observed to be arranged in a highly uniform fashion and the morphology of nanoparticles predicts high adsorption of the target gas, which may help in getting more response/sensitivity. The water contact angle image of SnO₂ film recorded is given as an inset of Fig. 2. The SnO₂ film with 96° water contact angle confirms hydrophobic nature (96° > 90°).

The three-dimensional (3-D) AFM images of SnO₂ and Au-SnO₂ surfaces were recorded (Fig. 3). The spherical-type morphology of SnO₂ sample is confirmed by AFM image. The AFM image exhibits 7 nm root mean square roughness (R_q) and 5 nm arithmetic average roughness (R_a) for SnO₂ sample whereas R_q is 10 and R_a is 8 nm for Au-SnO₂ sample. Au-SnO₂ film surface is rougher than SnO₂ which may be attributed to the presence of Au nanoparticles. Morphology and surface roughness affect on the gas sensing performance since different morphologies and different surface roughnesses offer different surface areas which provide active sites for gas adsorption and hence sensing output.

To confirm the noble metal sensitization on metal oxide sensing film, the EDS measurements were carried out at various places of sensor surface [5]. The quantitative analysis of EDS spectrum for sensitized film sample shows the presence of Sn, O and Au elements (Fig. 4). The atomic percentages of Sn, O and Au are found to be 23.74, 94.85 and 1.40, respectively. The high concentration of oxygen (O) is due to the stoichiometric ratio of Sn:O (1:2). The concentration of noble metal salt (Au) used in present work for sen-



a)



b)

Fig. 2. The field emission scanning electron micrograph images of; a) SnO₂ and b) Au sensitized SnO₂ films (respective surface contact angle measurement image as inset).

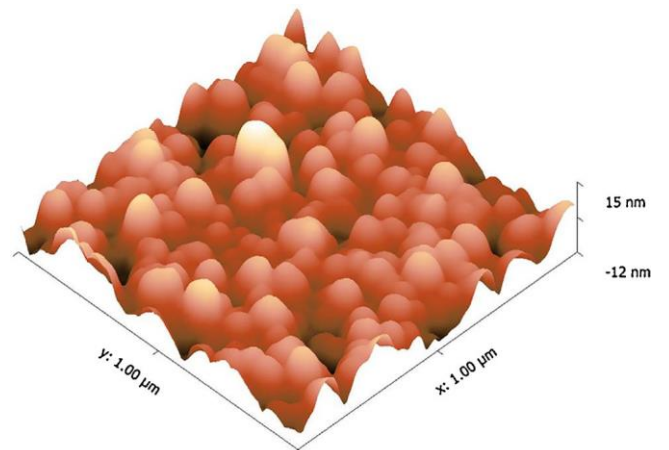
sitization was 0.001 M (1 mM), which is much lesser compared to noble metal (Pd) used for sensitization in previous report[5]. The presence of Au on/in the SnO₂ film surface is thus confirmed. Au nanoparticles and their cluster on the surface of SnO₂ film can be observed from FE-SEM image (Fig. 2 b). Average Au nanoparticle size is measured to be ~14 nm. The presence of Au nanoparticles on SnO₂ film can also be confirmed by UV-absorbance spectrum which is the inset of Fig. 4. The characteristic plasmon resonance absorbance peak of Au nanoparticles (533 nm) along with SnO₂ absorbance peak is observed in UV absorbance spectrum of Au sensitized SnO₂ film.

3.3. Optical properties

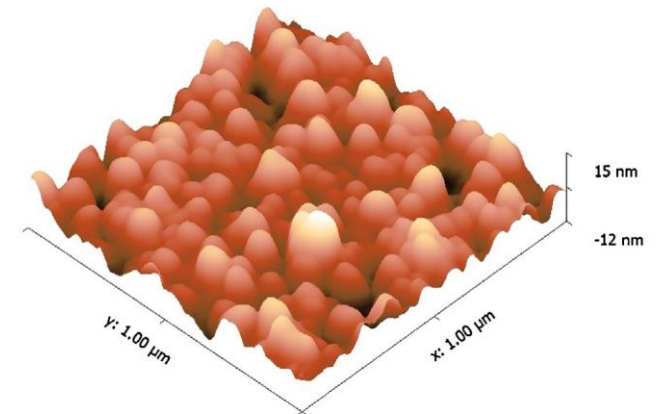
The band gaps of SnO₂ and Au-SnO₂ films were calculated from Tauc's plots. The Tauc's relation of photon energy ($h\nu$) with absorption coefficient (α) is given as [4]

$$\alpha = \frac{\alpha_0(h\nu - E_g)^n}{h\nu} \quad (3)$$

where, E_g is the band gap of material, $h\nu$ is the photon energy, α is absorption coefficient, α_0 is constant. The value of 'n' depends upon the transition type. The 'n' can have values 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively. The Tauc's plots are shown in Fig. 5. The linear absorption edge confirms direct band gap with



a)



b)

Fig. 3. Three-dimensional AFM images of; a) SnO₂ and, b) Au sensitized SnO₂ films.

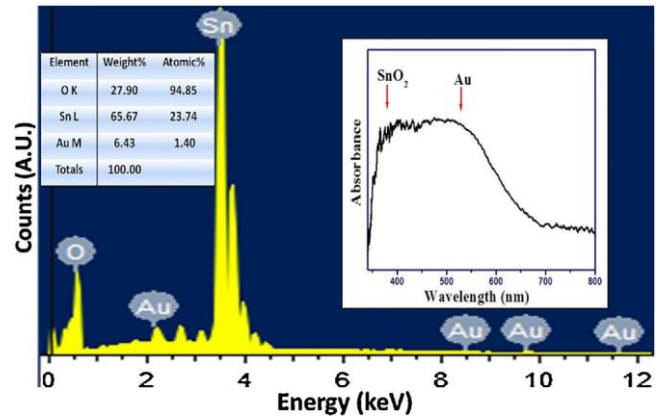


Fig. 4. EDS spectrum of Au sensitized SnO₂ film (with inset as UV-absorbance).

semiconducting nature of SnO₂ film. By extrapolating straight line portion up to photon energy axis (X-axis in Tauc's plot Fig. 5) to zero which corresponds to zero absorption coefficient value gives band gap. The band gap values for SnO₂ and Au-SnO₂ are estimated to be 3.2 eV and 3.15 eV, respectively. The lesser band gap of Au-SnO₂ may be attributed to the presence of Au nanoparticles, which creates allowed energy levels in between Fermi energy and conduction band of materials. The activation energy required for lesser band

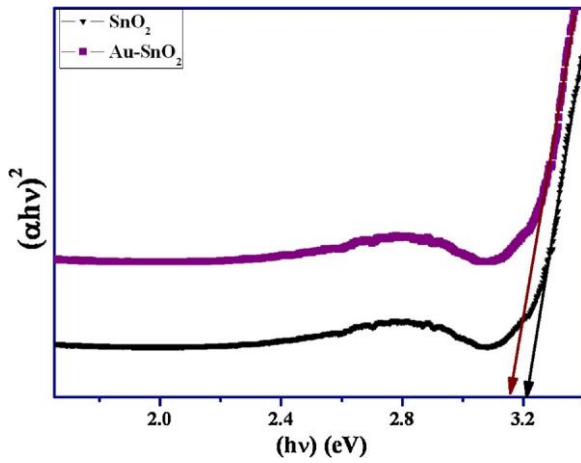


Fig. 5. Tauc's plots for SnO₂ and Au-SnO₂ films.

gap materials is less. This may lead to develop smaller operating temperature for said sensor. At lower operating temperature there is a high rate of gas adsorption and hence sensing performance can be the function of band gap energy.

3.4. LPG sensing properties

The LPG responses of pure SnO₂ and Au sensitized SnO₂ films as a function of operating temperature are shown in Fig. 6a) at the exposure of 520 ppm LPG concentration. The LPG response for unsensitized SnO₂ is increased up to 26% with increase in temperature up to 623 K and further it is decreased at 675 K, whereas for Au -sensitized SnO₂, a maximum response of 32% at relatively low temperature 598 K is achieved. The optimal working temperatures for SnO₂ and Au-sensitized SnO₂ films are found out to be 623 K and 598 K, respectively.

At low operation temperatures, gas molecules do not have enough thermal energy to react with the surface chemisorbed oxygen species, which results in low LPG response. The chemisorbed oxygen draws electrons from the conduction band of SnO₂ and a potential barrier to charge transport is developed. The potential barrier can be overcome due to the sufficient thermal energy obtained at higher temperatures, and sensing reaction leads to significant increase in the electron concentration. The gas response of a semiconductor metal oxide gas sensors depends on the speed of the surface chemical reaction of the crystallites and the diffusion speed of the gas molecules at the surface enhances. Since activation energy of gas sensing chemical reaction is higher, the higher temperature is required.

The LPG sensing response at lower temperature is restricted by the speed of the chemical reaction; it is restricted by the gas molecules diffusion speed at higher temperatures. The speed of chemical reaction and gas diffusion processes become equal at some intermediate temperature, and at that point, the sensor response reaches its maximum [27]. That intermediate operating temperature for unsensitized SnO₂ is 623 K and for Au surface sensitized SnO₂ film is 598 K. The selectivities of SnO₂ and Au-SnO₂ sensors toward LPG are given in Fig. 6b). As compared to other gases, the present sensor is observed to be quite selective.

3.5. LPG sensing mechanism for SnO₂ and Au-sensitized SnO₂

The gas sensing properties of metal oxide depend on the various process such as adsorption, desorption, and diffusion of gases inside crystal lattice. The LPG sensing mechanism is surface controlled; change in the resistance is controlled by the charged species and

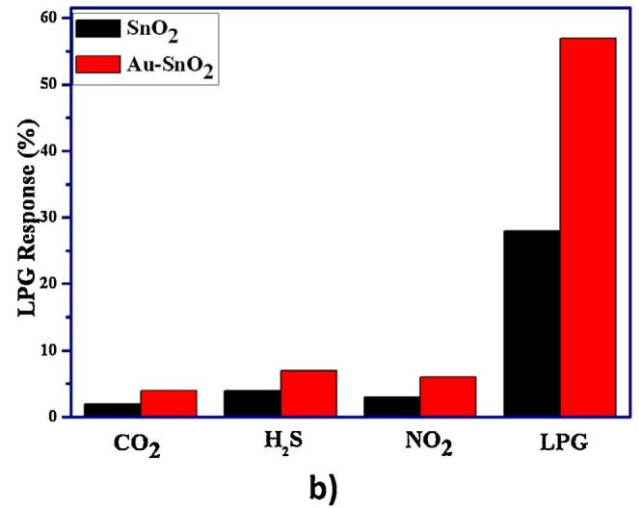
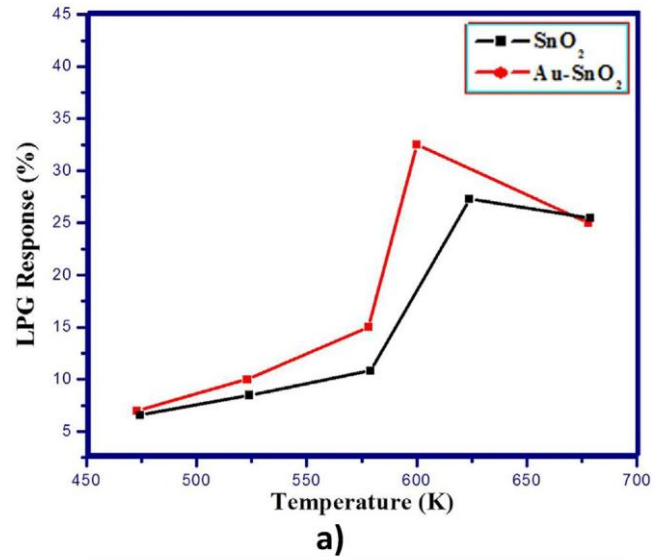


Fig. 6. a) LPG responses of the SnO₂ film and Au sensitized SnO₂ films upon exposure to 520 ppm of LPG at various temperatures. b) selectivity graphs for SnO₂ and Au-SnO₂ films.

amount of chemisorbed oxygen on the surface. The mechanism of LPG reaction proceeds through several intermediate steps and quite complex, which has not yet fully understood [28]. Prior to exposure of LPG, air oxygen gets adsorbed on the sensor surface at an operating temperature and draws electrons from the conduction band of the sensor material [29], that can be explained by the following reactions (4)–(6) [30]:



After saturation of the chemisorbed oxygen, the surface resistance of sensor material stabilizes. The electrical property or resistance of the sensing film changes due to any chemical reduction or oxidation process happens on sensor surface [29]. The LPG consists of hydrocarbons like CH₄, C₃H₈, C₄H₁₀, etc., and in these molecules, the reducing hydrogen species are bound to carbon atoms. Therefore, LPG dissociates less easily into reactive reducing components on the metal oxide surface. The overall reaction of

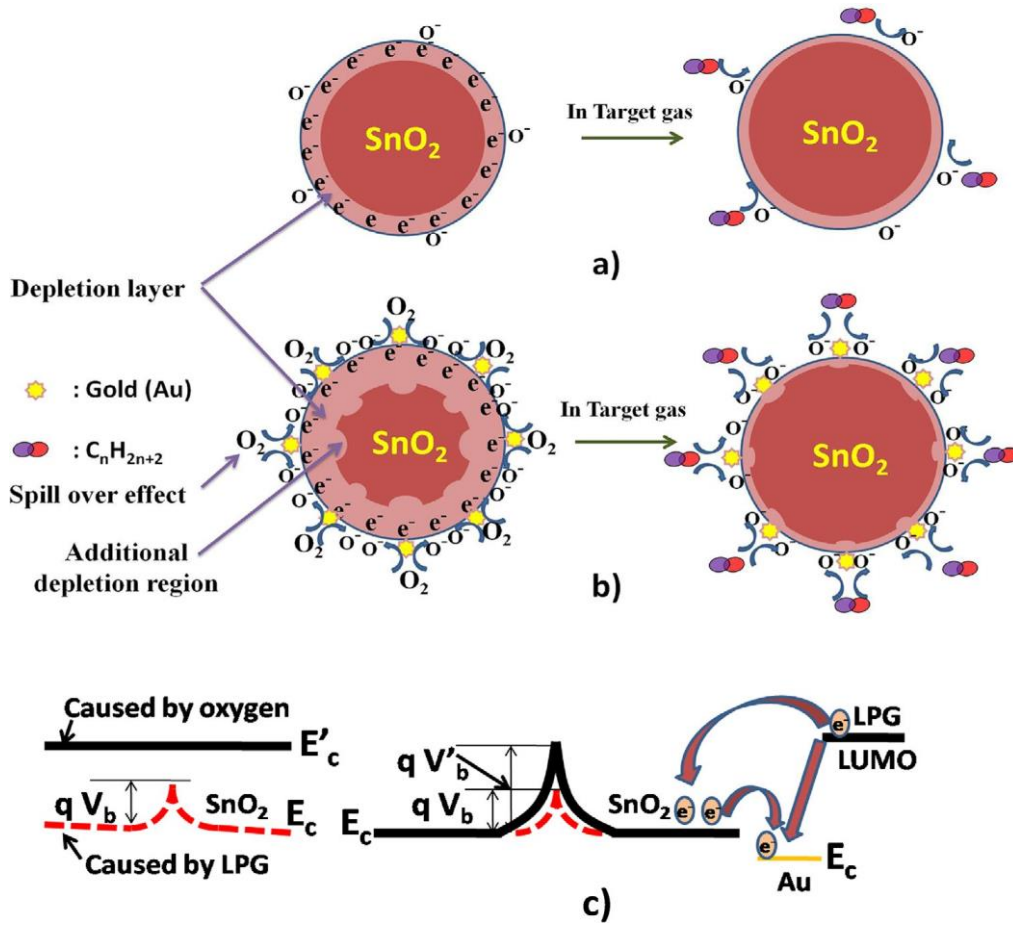
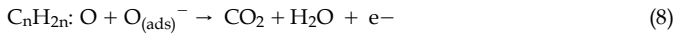
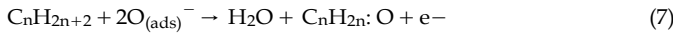


Fig. 7. Schematic diagram of LPG sensing mechanism of; a) unsensitized, b) Au-sensitized SnO₂ films, c) band structure change of sensor system on Au-sensitization.

LPG molecules with adsorbed oxygen can be explained as follows [27]:



where, $\text{C}_n\text{H}_{2n+2}$ represent the CH_4 , C_3H_8 and C_4H_{10} and $\text{C}_n\text{H}_{2n}\text{:O}$ represent partially oxidized intermediates on the SnO₂ surface. This reaction gives product CO_2 , H_2O and releases electrons back to the conduction band of sensing material, hence the resistance of the sensing material decreases with the exposure of LPG.

Noble metals are intentionally introduced to promote the receptor function and thus improve the sensing behaviours in terms of response, response/recovery times and selectivity for certain gases [31]. The metal catalytic additive increases the specific reactions rate on the metal oxide grain surface via modification of surface energy states and spill-over mechanism. The effects of the noble metals on the improvement of sensor response follow two types of mechanisms i.e. electric effect [32] and chemical effect [33,34]. A possible mechanism for enhancement in LPG response is schematically shown in Fig. 7. For the unsensitized SnO₂ film, Au nanoparticles on the surface are missing, chemisorbed oxygen molecules draw electrons from the SnO₂ so that it creates an electron depleted layer beneath the surface of SnO₂ nanoparticles (Fig. 7a). With the LPG exposure, oxygen concentration decreases, this suppresses the growth of electron depleted layer width. Whereas in the case of Au sensitized SnO₂ film, the change in electron depleted layer width is more remarkable due to electric and catalytic chemical effects during the exposure of LPG, and hence great enhancement in response towards LPG sensing

is observed. The electronic effect is associated with the creation of electron-depleted regions beneath the Au particles due to the flow of electrons from the conduction band of SnO₂ to Au particle; consequently increases an additional electron-depleted region. In electron-depleted region state Au particles on the surface of SnO₂ provides more active sites for oxygen adsorption and enhance the migration of adsorbed oxygen molecules onto SnO₂, which are less likely to adsorb oxygen molecules. Due to this spillover effect, the adsorption of oxygen species will be facilitated, which leads to increase in thickness of the electron-depleted layer, and flow of electrons in the underlying conduction channel will be significantly more suppressed (Fig. 7b). The similar explanation of schematic sensing mechanism for noble metal sensitized gas sensors has reported earlier [11,14]. The exposure of LPG readily expands the width of conduction channel, which further shows intensified sensing response signal. The band structure for the sensing system is shown in Fig. 7c [35]. The potential barriers and electric effect of noble metal have shown by their conduction energy band. The electron flow occurs from sensing material SnO₂ to Au sensitization (catalyst) because Au has lower conduction band bottom than SnO₂ and the work function of Au is higher than semiconducting metal oxide (SnO₂). When LPG is exposed, the LPG molecules react with sensor material, in the chemical reaction and then the electron from lower unoccupied molecular orbital (LUMO) of LPG (reducing gas) transfers to SnO₂ as well as to Au. Which lowers the sensor resistance and hence sensor response increases.

The transient LPG responses of unsensitized SnO₂ at 623 K and Au-sensitized SnO₂ film at 598 K on exposure of 780 ppm LPG are shown in Fig. 8. As the LPG molecule adsorb and react with pre

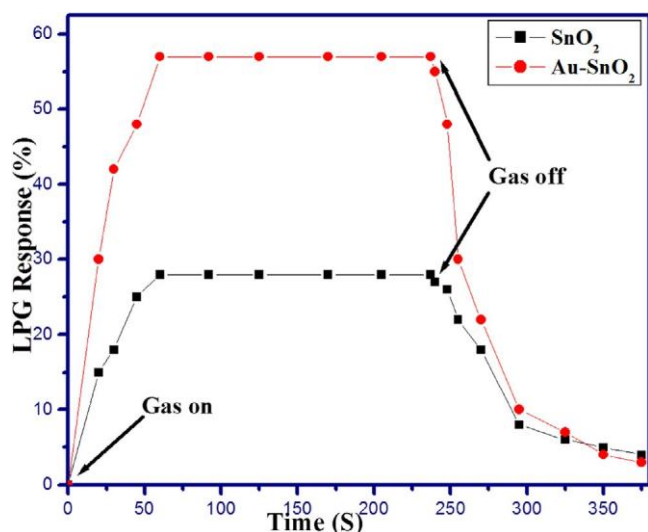


Fig. 8. The transient LPG responses for SnO_2 film at 623 K and Au-sensitized SnO_2 film at 598 K upon exposure to 780 ppm of LPG.

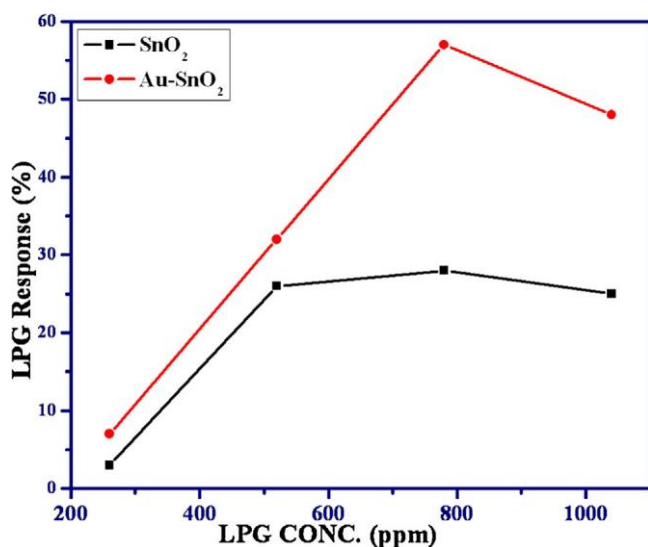


Fig. 9. Response curves of the SnO_2 film at 623 K and Au-sensitized SnO_2 film at 598 K upon exposure of various LPG concentrations.

chemi-adsorbed oxygen species, the gas response increases with time. After a specific time, the LPG response becomes constant due to saturation or equilibrium condition of LPG molecule adsorption with the sensor surface. When sensor system is exposed to an external (open) system the LPG molecules go under desorption which lowers down gas response. The time required for attaining maximum LPG response from the time when target LPG introduced in the testing chamber is called as response time. The rapid response time of 60 s is noted for the present sensor. The reproducibility and stability of the Au sensitized SnO_2 sensor was also measured by repeating the experiment many times.

3.6. LPG concentration effect on sensing

The effect of LPG concentration on the sensor responses of unsensitized SnO_2 at 623 K temperature and Au-sensitized SnO_2 at 598 K temperature are shown in Fig. 9. The number of LPG molecules react with sensor surface is increased with LPG concentration, which leads to increase in the sensor response. LPG response for both samples is increased with the increase in LPG

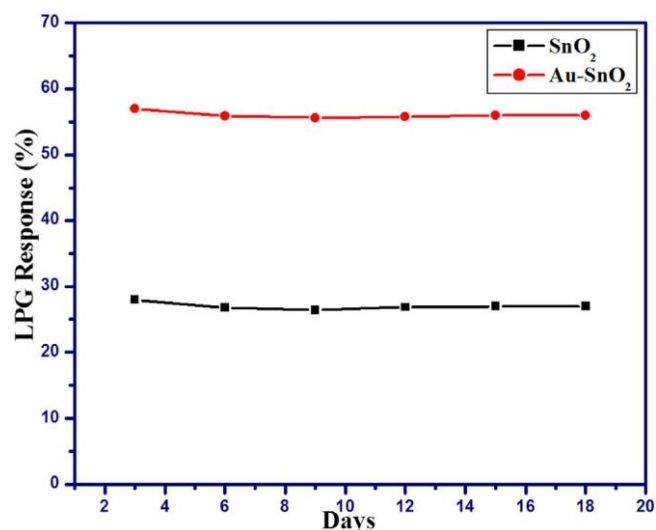


Fig. 10. Stability tests of present sensors.

concentration. Both samples show the highest response at 780 ppm LPG concentration level. The maximum LPG response values noted for unsensitized SnO_2 is 28% and for Au sensitized SnO_2 is 57% for 780 ppm LPG concentration.

The stabilities of sensors were checked by testing LPG response multiple times (Fig. 10). Both sensors show approximately good stability. LPG response and operating temperature for Au- SnO_2 sensor are better as compared to previous report [11].

4. Conclusions

In this work, the LPG sensing response of sprayed pristine and Au-sensitized SnO_2 film have been studied and reported. Maximum LPG response found for unsensitized SnO_2 is 28% at 598 K temperature and for Au sensitized SnO_2 is 57% for 780 ppm gas concentration at 598 K operating temperature. The mechanism for enhanced LPG sensing due to Au sensitization is thoroughly discussed. These sensors exhibit the potential to detect lesser gas concentration than 1000 ppm (Permissible exposure Limit (PEL) for LPG as specified by NIOSH and OSHA standards) with high sensing response. Au sensitized SnO_2 film demonstrates remarkable LPG sensing properties, which makes it as promising high gas response sensor material in particular when portable sensor device is targeted.

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